Molecular Modeling
The Introduction

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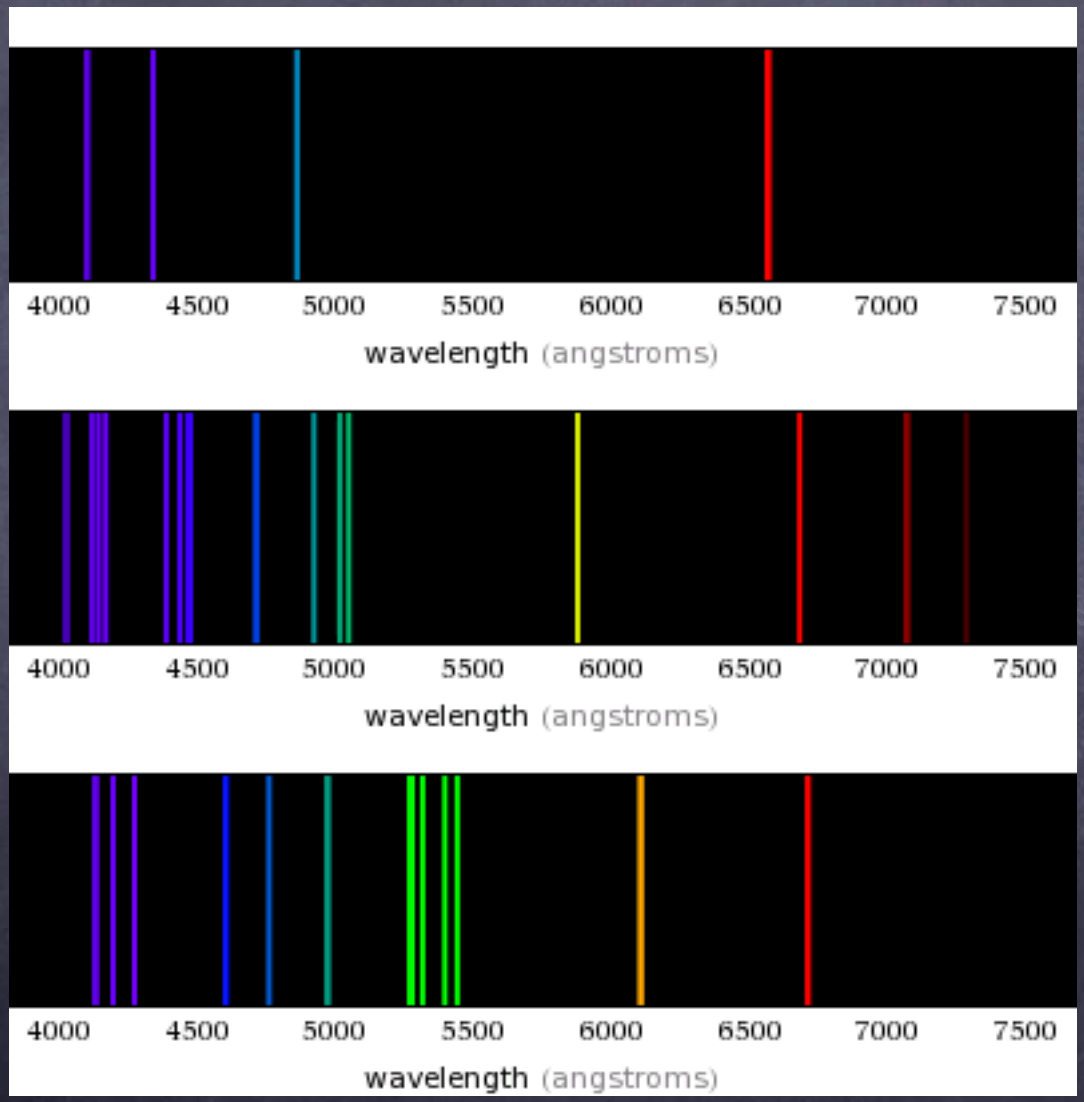
Atomic Emission Spectra

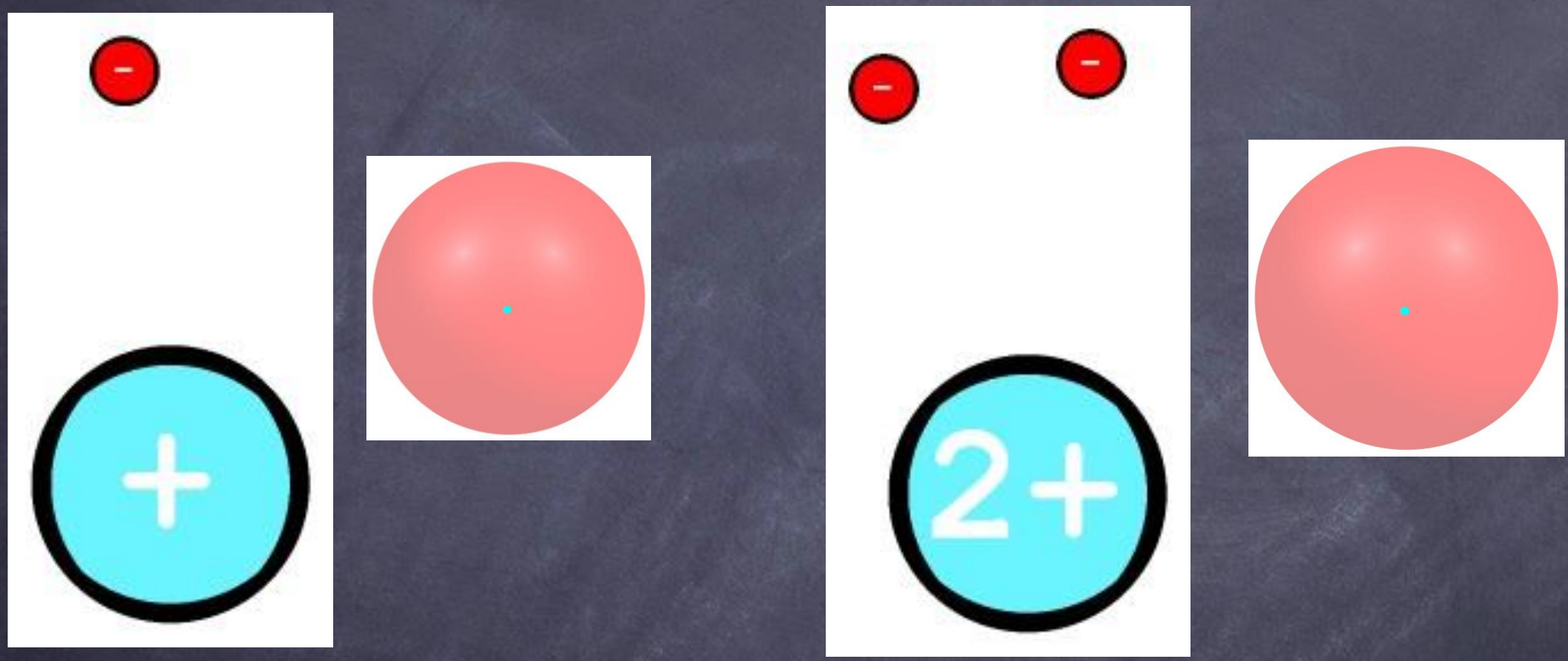
- H
- He
- Li



discrete and narrow

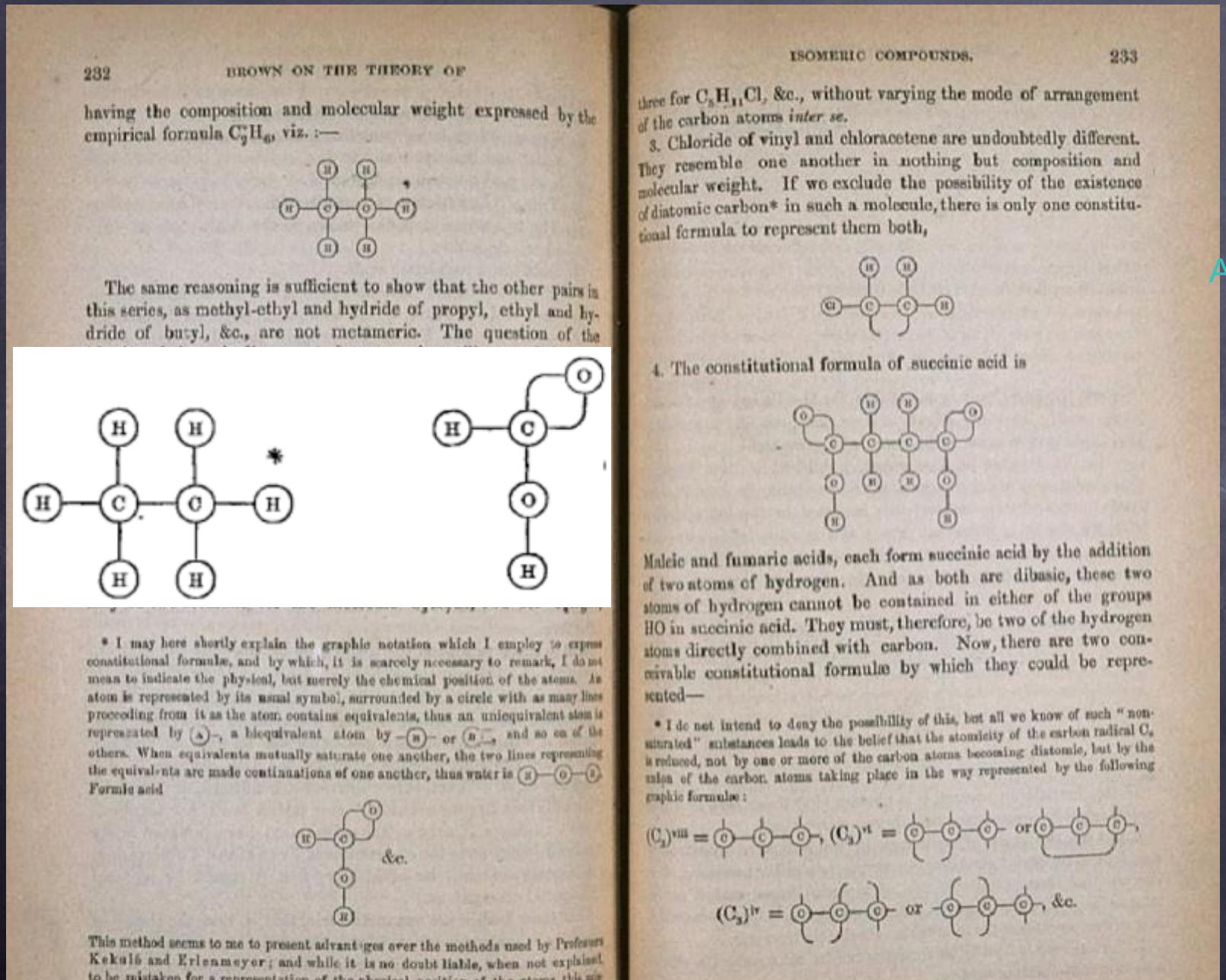
http://www.wolframalpha.com/

Atomic Models



- Bohr model $E= -Ze^2/r= -13.6Z^2/n^2$
- electronic structure: labeling electrons with quantum numbers

Molecular Models



232 BROWN ON THE THEORY OF

having the composition and molecular weight expressed by the empirical formula $C_2''H_6$, viz. :—

The same reasoning is sufficient to show that the other pairs in this series, as methyl-ethyl and hydride of propyl, ethyl and hydride of butyl, &c., are not metameric. The question of the

* I may here shortly explain the graphic notation which I employ to express constitutional formulæ, and by which, it is scarcely necessary to remark, I do not mean to indicate the physical, but merely the chemical position of the atoms. An atom is represented by its usual symbol, surrounded by a circle with as many lines proceeding from it as the atom contains equivalents, thus an unequivalent atom is represented by (A)–, a bicquivalent atom by –(B)– or (B)<, and so on of the others. When equivalents mutually saturate one another, the two lines representing the equivalents are made continuations of one another, thus water is (H)—(O)—(H). Formic acid

&c.

This method seems to me to present advantages over the methods used by Professors Kekulé and Erlenmeyer; and while it is no doubt liable, when not explained, to be mistaken for a representation of the chemical position of the atoms, this mis

ISOMERIC COMPOUNDS. 233

three for $C_3H_{11}Cl$, &c., without varying the mode of arrangement of the carbon atoms *inter se*.

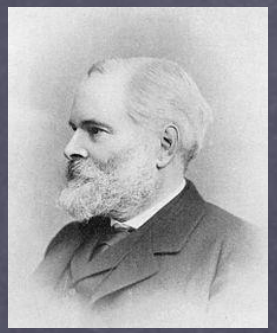
3. Chloride of vinyl and chloracetene are undoubtedly different. They resemble one another in nothing but composition and molecular weight. If we exclude the possibility of the existence of diatomic carbon* in such a molecule, there is only one constitutional formula to represent them both,

4. The constitutional formula of succinic acid is

Maleic and fumaric acids, each form succinic acid by the addition of two atoms of hydrogen. And as both are dibasic, these two atoms of hydrogen cannot be contained in either of the groups HO in succinic acid. They must, therefore, be two of the hydrogen atoms directly combined with carbon. Now, there are two conceivable constitutional formulæ by which they could be represented—

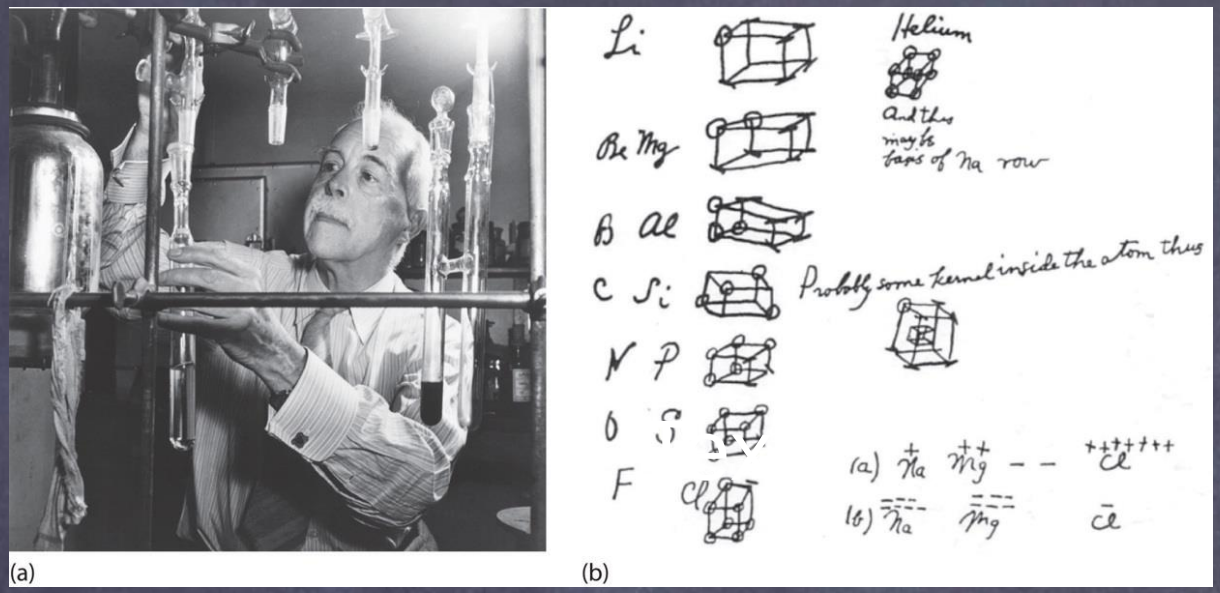
* I do not intend to deny the possibility of this, but all we know of such "non-saturated" substances leads to the belief that the atomicity of the carbon radical C_2 is reduced, not by one or more of the carbon atoms becoming diatomic, but by the union of the carbon atoms taking place in the way represented by the following graphic formulæ:

$(C_2)^{viii} =$ (C)—(C)—(C), $(C_2)^{vi} =$ (C)—(C)—(C) or (C)—(C)—(C), $(C_2)^{iv} =$ (C)—(C)—(C) or (C)—(C)—(C), &c.



Alexander Crum Brown
1864

The Idea of Chemical Bond

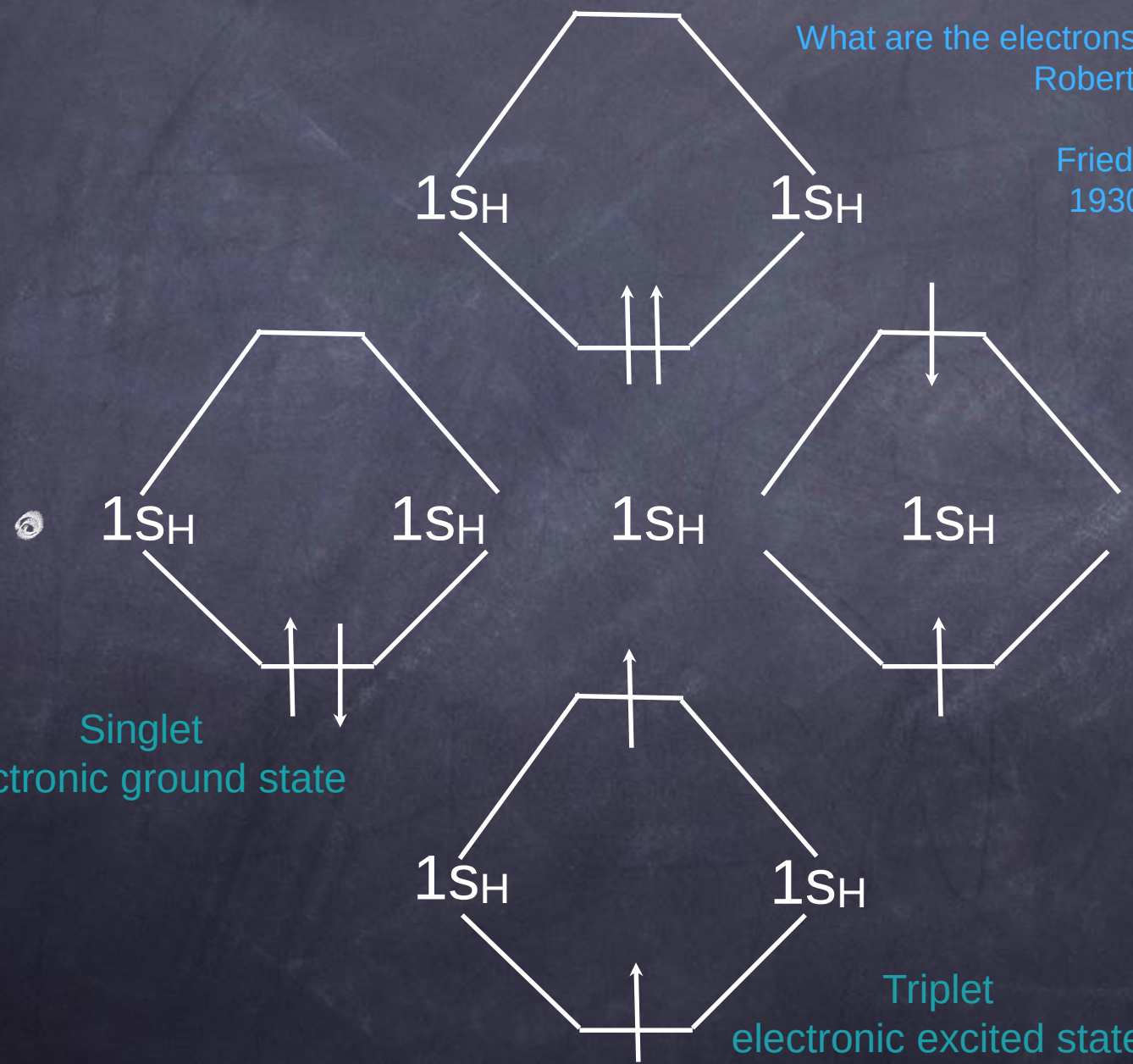


- Frankland, Van't Hoff and le Bel (1857: electrical nature of chemical bond)
- Van''t Hoff (1877 , The arrangement of atoms in SPACE , tetrahedrally directed bonds in Carbon, optical activity of tartaric acid)
- G.N Lewis (1902, electrons are responsible to bind atoms together) ,
- Linus Pauling (1931, The nature of Chemical Bond)

Brian T.Sutcliffe,Int.J.Quant,Chem,vol:58,pages645-655,year:1996

Molecular Orbital Theory

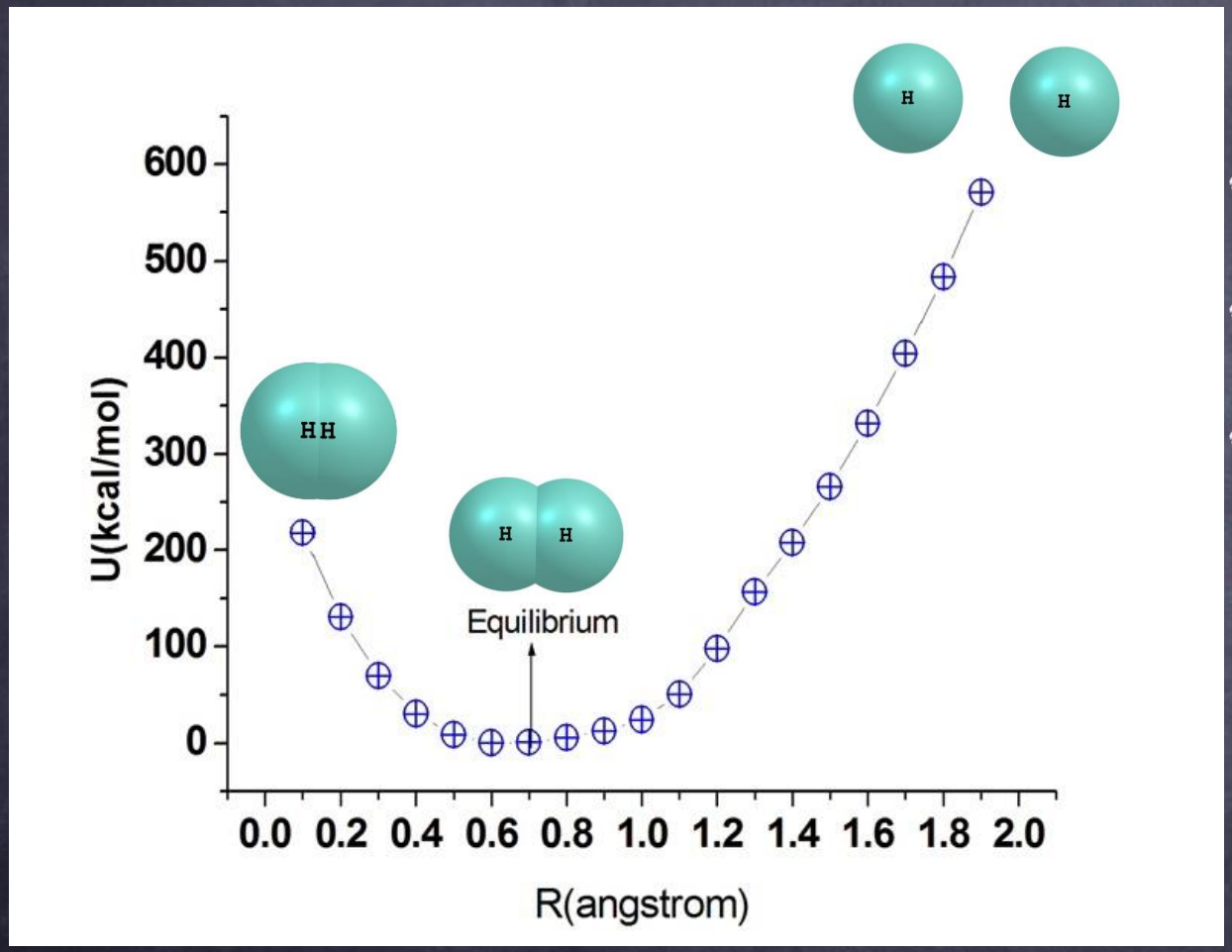
What are the electrons really doing in Molecules?
Robert S.Mulliken
and
Friedrich Hund
1930s-1940s



Singlet
electronic ground state

Triplet
electronic excited state

Molecular Mechanics



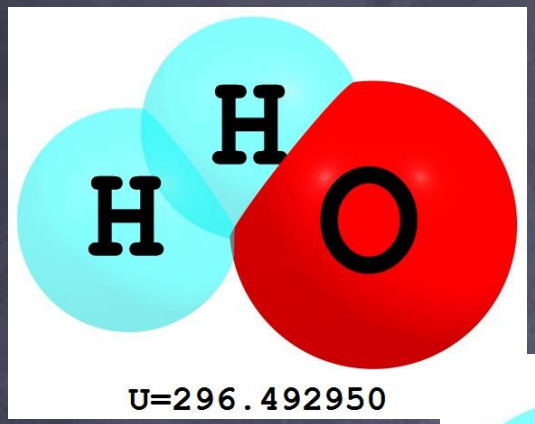
- The Idea of Force Field,
- Potential Energy Surface (PES)
- Minimization of Energy

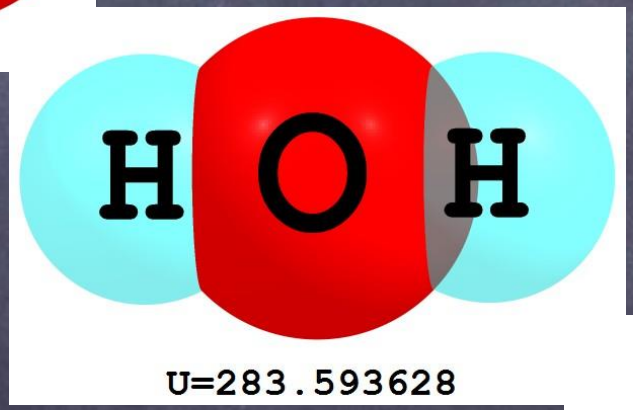
$$U=K(r-A)^2$$

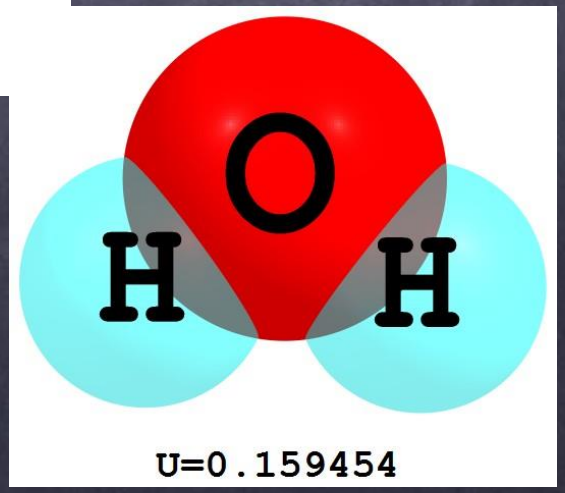
A= an experimental parameter

Norman L. Allinger (1970s,1980s)
Graphite. A Molecular Mechanics Treatment, J.Comput.Chem, No:3,Pages:257-260, year:1980

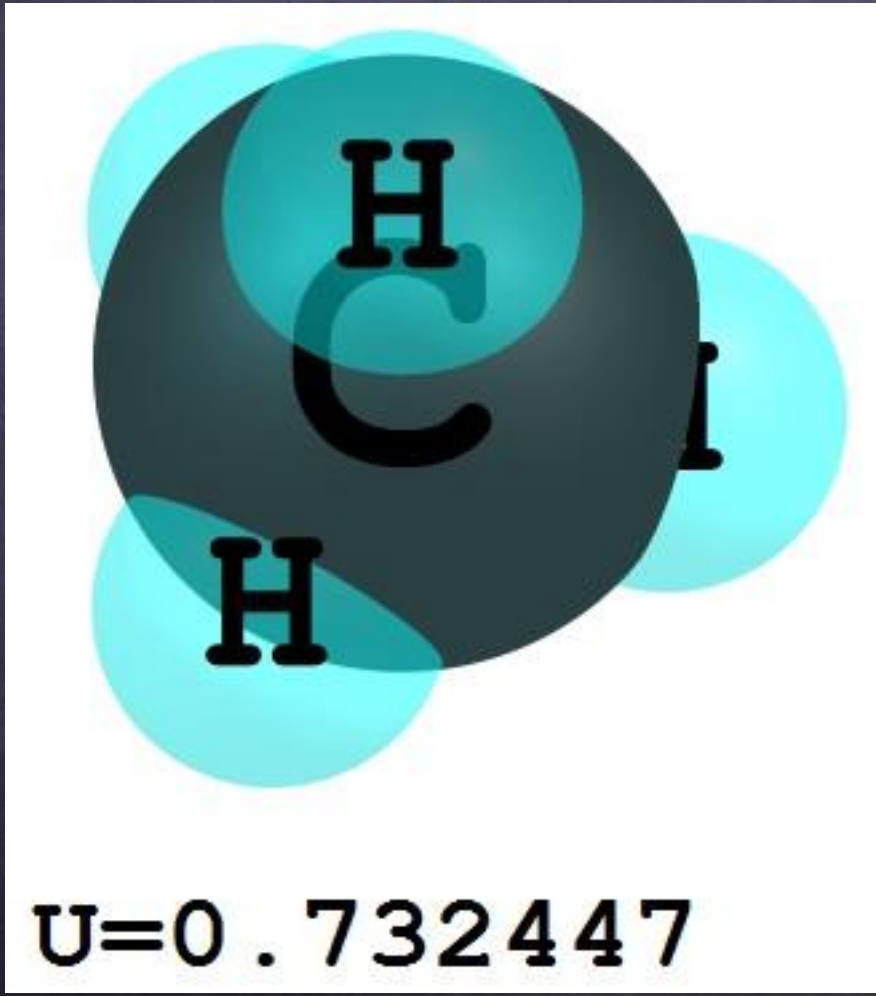
Example1:The Water

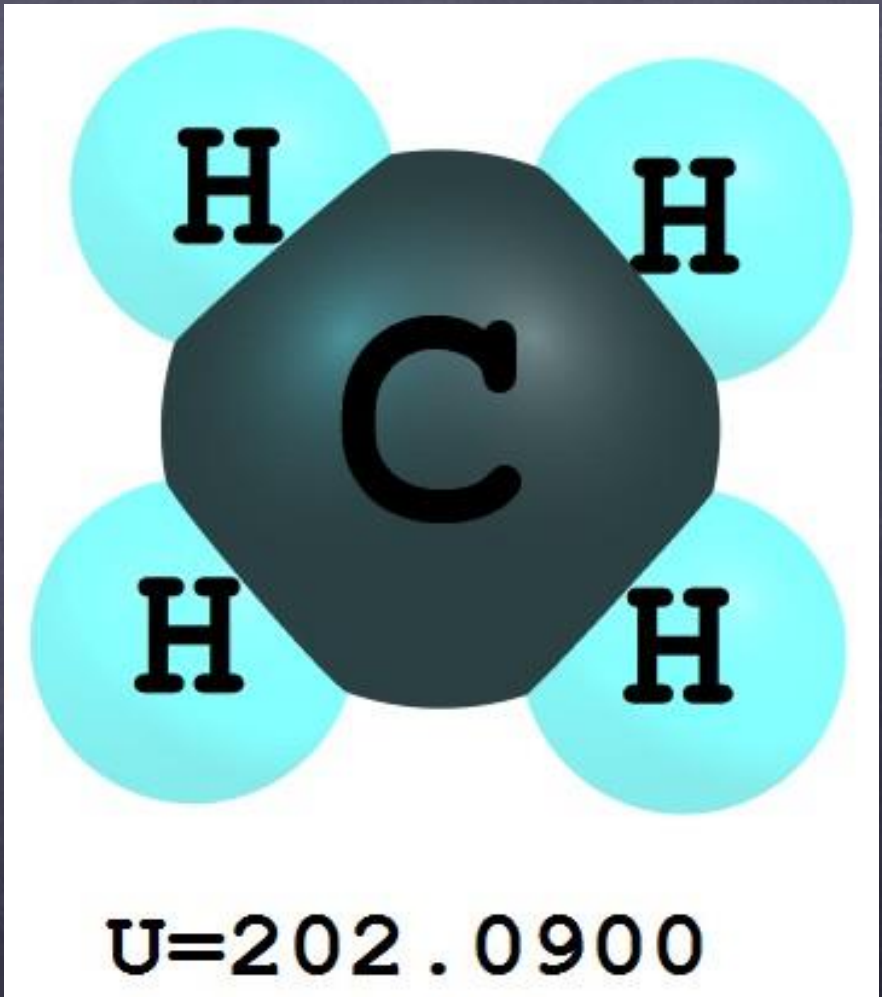




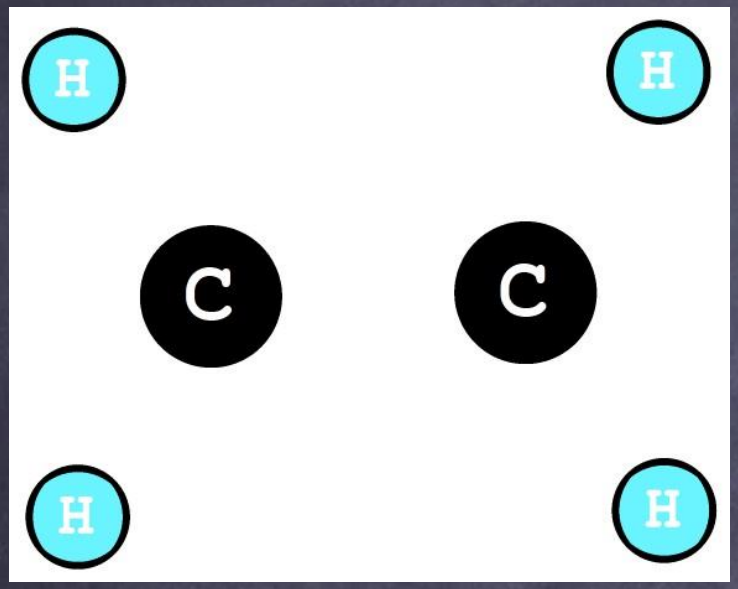


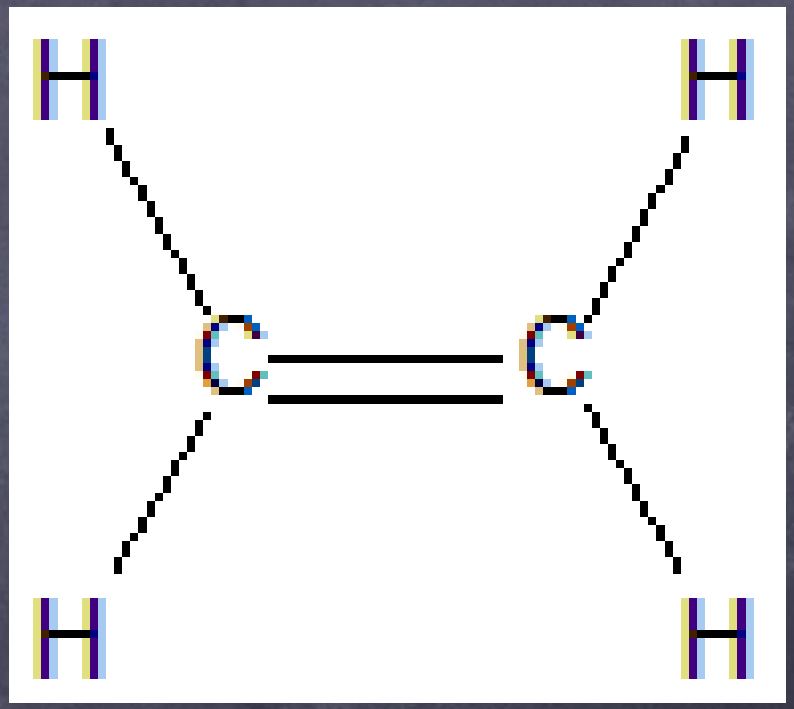
Example2:The Methane





Geometry and Structure





C	-0.164207364	0.000000000	-1.133069988
C	-0.164207364	0.000000000	0.197088012
H	-0.164207364	0.923341000	-1.706019988
H	-0.164207364	-0.923341000	-1.706019988
H	-0.164207364	0.923341000	0.770038012
H	-0.164207364	-0.923341000	0.770038012

- Energy Minimization->Geometry Optimization

Molecular Modeling

Modeling the Molecules with PC

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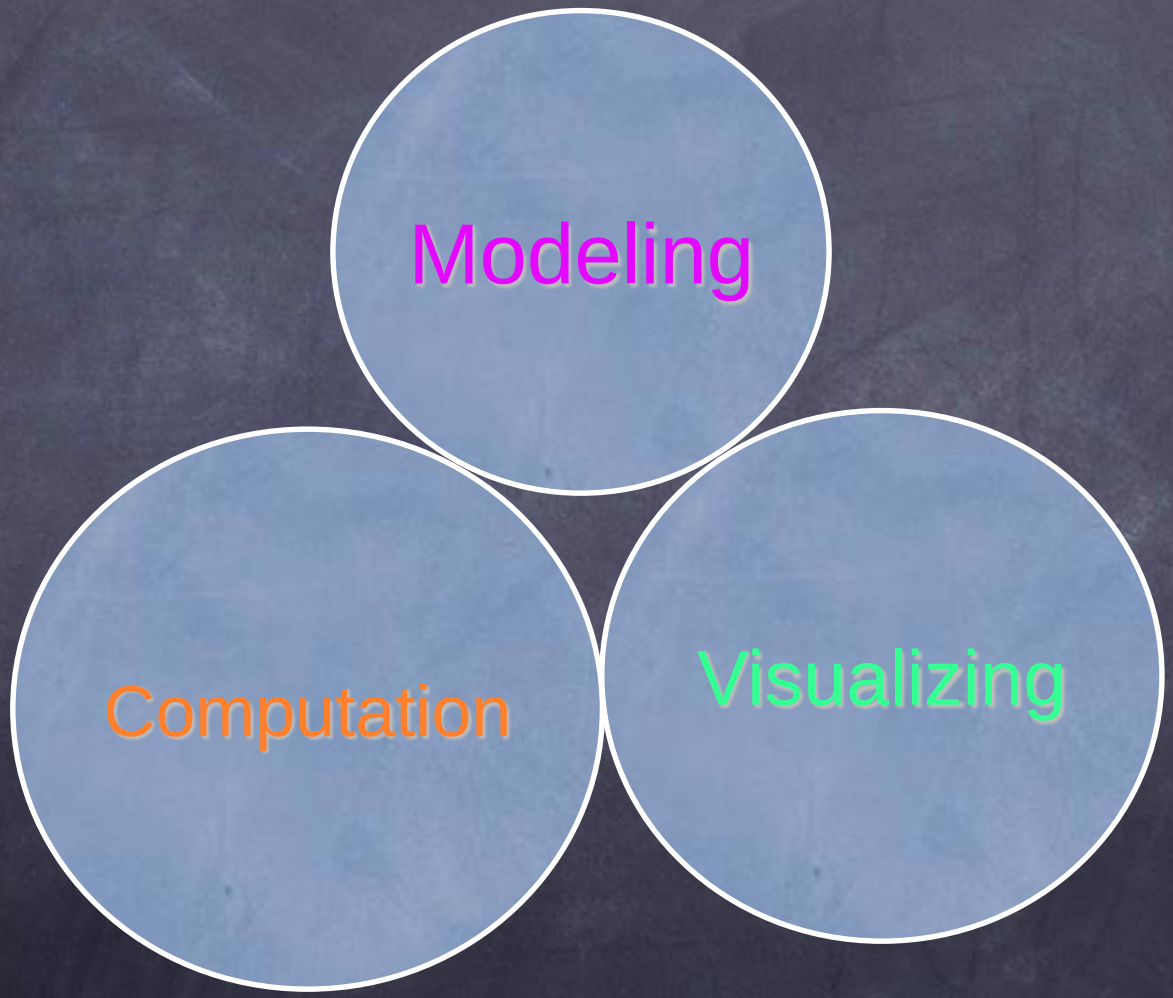
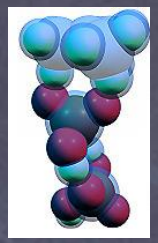
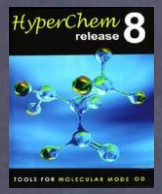
Rules

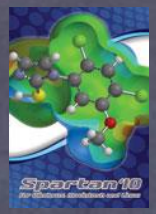
- Any atomic or molecular model has its own limitations.
- we do not discard any model
- Our starting point should be always the simplest model
- The goal is to get the desirable results within the hardware and software limitations in reasonable time
- Molecular Modeling is an Art

Modeling Triangle



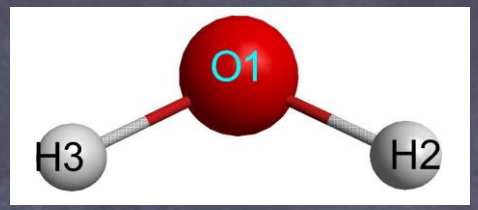
Model Builders



- MacMolPlt http://www.scl.ameslab.gov/MacMolPlt
- ChemCraft http://www.chemcraftprog.com
- HyperChem http://www.hyper.com
- Chemoffice http://scistore.cambridgesoft.com
- Spartan http://www.wavefun.com/products/spartan.html

Cartesian Coordinate and Z-Matrix



- Cartesian coordinates

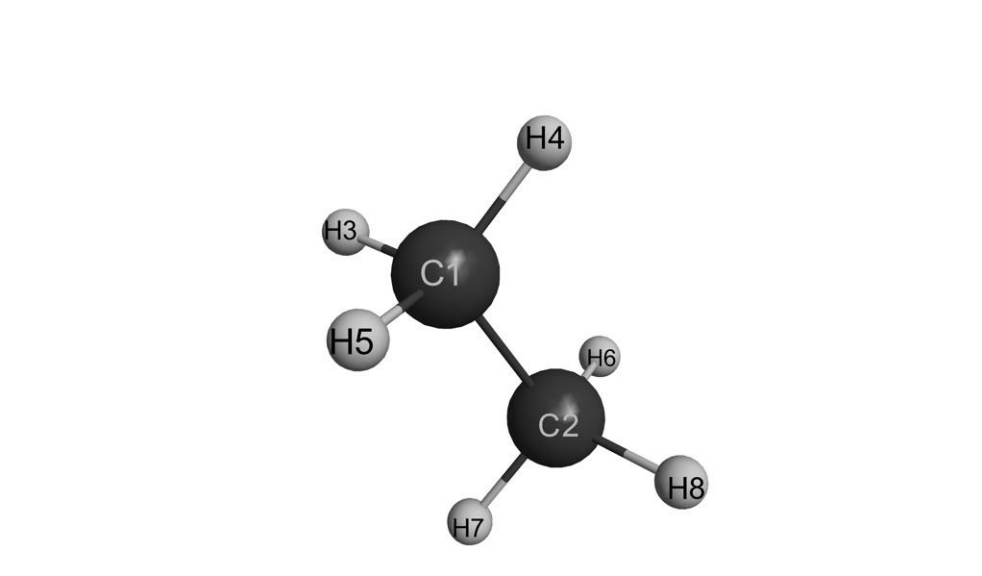
O	8.0	-0.20784609	-0.12990381	0.00000000
H	1.0	-0.20784609	0.97009617	0.00000000
H	1.0	-0.20784609	-0.49657050	1.03708994

- Z-Matrix

```
O
H  1   1.10000
H  1   1.10000  2 109.4712
```

Molecular Symmetry

```
C
C  1   1.54000
H  1   1.14000  2 109.4712
H  1   1.14000  3 109.4712  2 120.0000
H  1   1.14000  3 109.4712  4 120.0000
H  2   1.14000  1 109.4712  4 -60.0000
H  2   1.14000  6 109.4712  1 120.0000
H  2   1.14000  6 109.4712  7 120.0000
```




```
C
C  1   1.54000
H  1   1.14000  2 109.4712
H  1          3        2 120.0000
H  1          3        4
H  2          1        4 -60.0000
H  2          6        1
H  2          6        7
```

Molecular Modeling

Quantum Chemistry Calculations with PC

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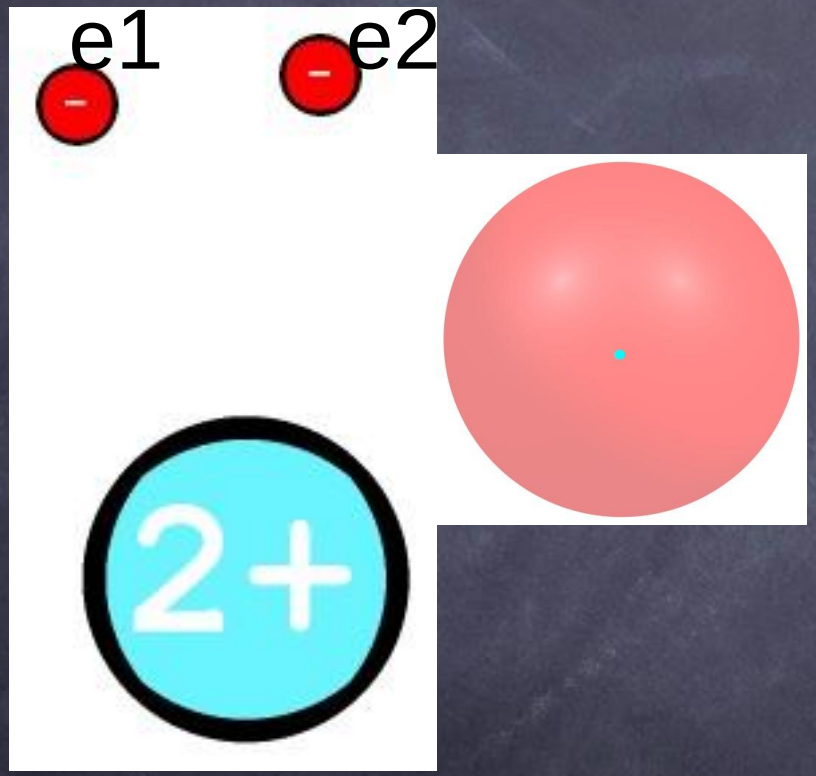
Quantum Mechanics

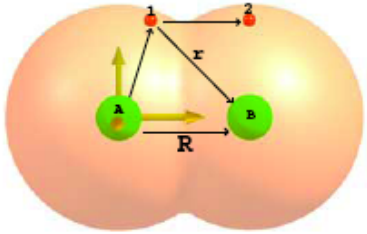


$$\{-\frac{1}{2}\nabla_1^2 + V[\psi_2]\}\psi_1 = \varepsilon_1\psi_1$$

$$\{-\frac{1}{2}\nabla_2^2 + V[\psi_1]\}\psi_2 = \varepsilon_2\psi_2$$

$$V[\psi_1] = -\frac{Z}{r} + \int \frac{\psi_1\psi_2^*}{r_{12}}$$

- electrons correct the motion of each other



$$\hat{H} = \hat{H}^e + \hat{T}$$

$$\hat{T} = (\frac{-\hbar^2}{2M_a}\nabla_a^2) + (\frac{-\hbar^2}{2M_b}\nabla_b^2)$$

$$\hat{H}^e = (\frac{-\hbar^2}{2}\sum_{i=1}^{N}\nabla_i^2) + (\sum_i^N -\frac{Z_a}{|\vec{r}_{ia}|}) + (\sum_i^N -\frac{Z_b}{|\vec{r}_{ib}|}) + (\sum_{i<j}\frac{1}{|\vec{r}_{ij}|}) + (\frac{Z_a Z_b}{|\vec{R}|})$$

$$\hat{H}\mathbf{\Psi}(\mathbf{r}\,|\,\mathbf{R}) = E\mathbf{\Psi}(\mathbf{r}\,|\,\mathbf{R})$$

$\mathbf{r}$: *electrons* coordinate including spin $\qquad$ $\mathbf{R}$: Nuclie coordinate

$$\hat{H}^e\psi_k^e(\mathbf{r}\,|\,\mathbf{R}) = E_k^e\psi_k^e(\mathbf{r}\,|\,\mathbf{R})$$

$\mathbf{\Psi}_{gr}(\mathbf{r}\,|\,\mathbf{R}) = \psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})$ Approx 1, gr : ground electronic state

$\chi_{gr}(\mathbf{R})$ = nuclie motion wave function

$$\langle\psi_{gr}^e\,|\,\psi_{gr}^e\rangle = 1 = \int_{\mathbf{r}}\psi_{gr}^{*,e}\psi_{gr}^e d^n\mathbf{r}$$

$$\hat{H}\mathbf{\Psi}_{gr}(\mathbf{r}\,|\,\mathbf{R}) = \hat{H}\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R}) = E\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})$$

$$\int_{\mathbf{r}}\psi_{gr}^{*,e}\hat{H}\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r} = \int_{\mathbf{r}}\psi_{gr}^{*,e}E\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r}$$

$$\int_{\mathbf{r}}\psi_{gr}^{*,e}(\mathbf{r}\,|\,\mathbf{R})(\hat{H}^e + \hat{T})\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r} = E\chi_{gr}(\mathbf{R})\int_{\mathbf{r}}\psi_{gr}^{*,e}\psi_{gr}^e d^n\mathbf{r}$$

$$\{\int_{\mathbf{r}}\psi_{gr}^{*,e}(\mathbf{r}\,|\,\mathbf{R})\hat{H}^e\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r}\} + \{\int_{\mathbf{r}}\psi_{gr}^{*,e}(\mathbf{r}\,|\,\mathbf{R})(\hat{T})\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r}\} = E\chi_{gr}(\mathbf{R})$$

$$\int_{\mathbf{r}}\psi_{gr}^{*,e}(\mathbf{r}\,|\,\mathbf{R})\hat{T}\psi_{gr}^e(\mathbf{r}\,|\,\mathbf{R})\chi_{gr}(\mathbf{R})d^n\mathbf{r} = \int_{\mathbf{r}}\psi_{gr}^{*,e}\hat{T}\psi_{gr}^e\chi_{gr}d^n\mathbf{r} = \int_{\mathbf{r}}\psi_{gr}^{*,e}(\frac{-\hbar^2}{2M_a}\nabla_a^2 + \frac{-\hbar^2}{2M_b}\nabla_b^2)\psi_{gr}^e\chi_{gr}d^n\mathbf{r}$$

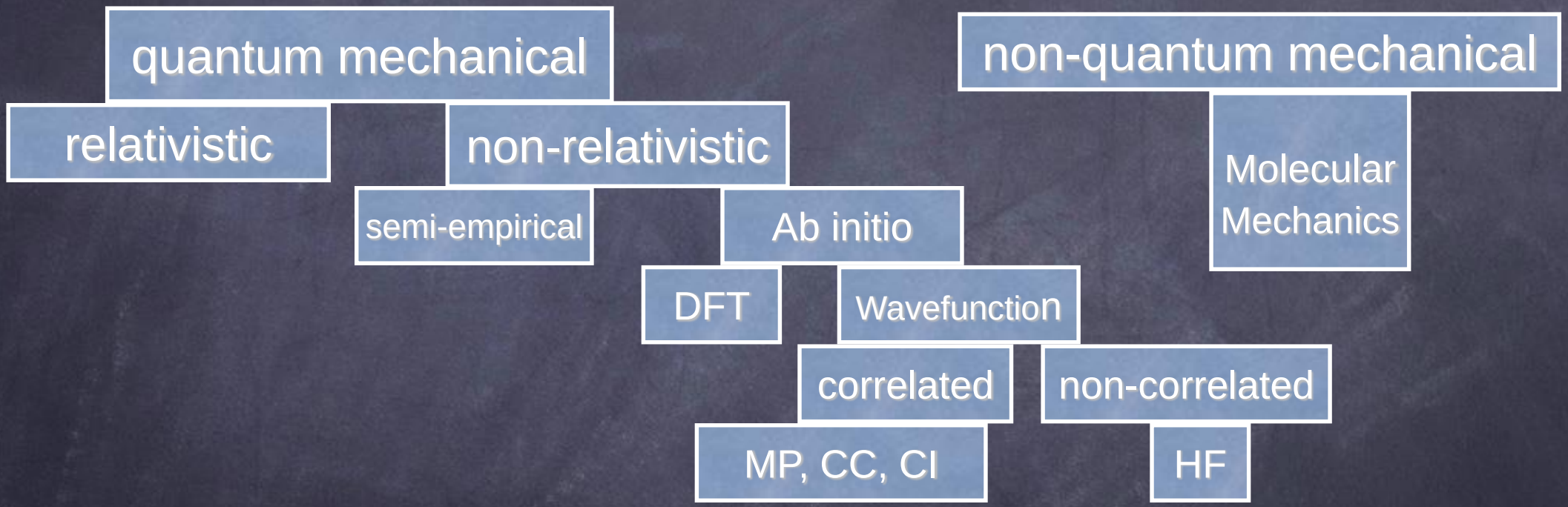
$$= \int_{\mathbf{r}}\psi_{gr}^{*,e}(\frac{-\hbar^2}{2M_a}\nabla_a^2)\psi_{gr}^e\chi_{gr}d^n\mathbf{r} + \int_{\mathbf{r}}\psi_{gr}^{*,e}(\frac{-\hbar^2}{2M_b}\nabla_b^2)\psi_{gr}^e\chi_{gr}d^n\mathbf{r} = \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(\psi_{gr}^e\nabla_a^2\chi_{gr} + \chi_{gr}\nabla_a^2\psi_{gr}^e + 2\nabla_a\psi_{gr}^e\nabla_a\chi_{gr})\}d^n\mathbf{r}$$

$$+ \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(\psi_{gr}^e\nabla_b^2\chi_{gr} + \chi_{gr}\nabla_b^2\psi_{gr}^e + 2\nabla_b\psi_{gr}^e\nabla_b\chi_{gr})\}d^n\mathbf{r}$$

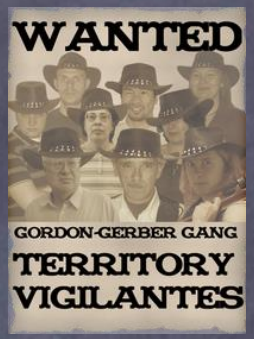
$$= \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(\psi_{gr}^e\nabla_a^2\chi_{gr})\}d^n\mathbf{r} + \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(\psi_{gr}^e\nabla_b^2\chi_{gr})\}d^n\mathbf{r} + \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(\chi_{gr}\nabla_a^2\psi_{gr}^e)\}d^n\mathbf{r} + \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(\chi_{gr}\nabla_b^2\psi_{gr}^e)\}d^n\mathbf{r}$$

$$+ \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_a}(2\nabla\psi_{gr}^e\nabla_a\chi_{gr})\}d^n\mathbf{r} + \int_{\mathbf{r}}\psi_{gr}^{*,e}\{\frac{-\hbar^2}{2M_b}(2\nabla_b\psi_{gr}^e\nabla_b\chi_{gr})\}d^n\mathbf{r}$$

Grand Classification of the Models



The Quantum Chemistry Packages



- PCGAMESS
- GAUSSIAN
- GAMESS-US
- MOLPRO
- etc

Molecular Modeling

HKU Molecular Modeling Shared Facilities

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HKU Supercomputer Infrastructure

- HPC Power

http://www.its.hku.hk/services/research/hpc/hpcpower

178 nodes, 32 bit Linux Cluster, each node: dual core Xeon 2.8-3GHz CPUs, 2Gb of RAM, 40GB HDD

- HPC Power2

http://www.its.hku.hk/services/research/hpc/hpcpower224 Nodes, 64bit Linux Cluster, each node: two quad-core Xeon 3GHz CPUs, 8Gb RAM,

- Gridpoint

http://www.its.hku.hk/services/research/hpc/gridpoint/userguide
(in Feb-March 2013, SAL upgraded the Gridpoint with new and advanced high speed Hard disks 6TB->21TB, SAL has 15TB HDD capacity

- Do you want to visit with Gridpoint?

Quantum Chemistry Packages

- http://www.its.hku.hk/services/research/hpc/software/list
- GAUSSIAN
- GAMESS-US
- GROMACS
- MATHEMATICA
- MATLAB

Applying for Account

- HKU portal account/Computer Information Services/Central IT services/Apply for Facilities-Services/
- High Performance Computing Cluster (hpcpower) Account Application (for Non-TOSI Staff/Students)
- High Performance Computing Cluster (hpcpower) Account Application (for TOSI Staff)